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ANALYSIS OF REACTION RATES BY COMPUTER METHODS

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TECHNICAL REPORT

72-38-CE

EVALUATION OF REACTION RATES

BY

COMPUTER METHODS

by

Matthew L. Herz

November 1971

i-c

FOREWORD

The proper statistical analysis of rate data necess.tates tedious and often complex calculations involving numerous data points. These manipulations can now be carried out easily and rapidly by digital computers.

The programs presented here make it practical to carry out the statistical analysis of kinetic data as routine part of a laboratory program, permitting a more complete evaluation of essential chemical properties. The programming was prepared and utilized in the investigation of compounds for use in the eye protection program. The work was performed in the Flame and Thermal Protection Section of the Chemical Modification of Textiles Branch of the Clothing and Personal Life Support Equipment Laboratory under Evaluation of Chemicals for Optical Shutters - Flashblindness Protection Project 1J662708DJ40-30. Most of the work was carried out in the period April to July 1971.

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13. ABSTRACT

A set of Fortran IV programs successfully used for analysis of chemical rate data are described. The programs utilize both the method of integration and that of differentiation to assign reaction orders, rate constants, and estimates of uncertainty. Highly reliable results can be obtained by use of these methods in combination.

Experimental data, consisting of time and concentration-dependent variables, are analyzed to produce the constants characteristic of the reaction being studied. The Fortran IV programs, written for a GE 200 series machine, are described. Details of use, input and output format, and program limitations are given.

i-A

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Computer Programming	8				10	
Data Analysis	4					
Fortran	10					
Integration			8			
Differentiation			8			
Chemical Kinetics			7, 10			
Concentration						
Temperature			6			
Pressure			6			
Evaluation			6		8	
Chemical Properties					9	
Investigations					4	
Compounds					4	
Visual Perception					4	

I-B

CONTENTS

1. INTRODUCTION

The rates of chemical reactions and the factors upon which they depend are studied quantitatively using the techniques of chemical kinetics. Laboratory studies of the effects of concentration, temperature, and pressure on reaction rates may lead to conclusions having practical applications or, once relationships between velocities of reactions and various controlling factors have been determined, more fundamental conclusions about reaction mechanisms may be arrived at by interpretation of the empirical laws observed in the laboratory.

In our investigation of the triarylmethane leuconitriles for use in nuclear flashblindness protection devices, it is necessary to determine the kinetics of the fading reaction of the leuconitriles. Once we know these rates and the factors affecting them a system which returns to the desired degree of transparency in an optimum period of time can be designed.

This report concerns the application of computer techniques to problems of chemical kinetics, that is, to elucidate the mechanisms of simple irreversible chemical reactions. Programs which are presently available for evaluation of kinetic data are generally of two types. The first type includes those that use the simplest least squares analysis and/or are applicable only to simple restricted cases.[1-4] Although some of these programs use advanced statistical methods, each of them is applicable only to chemical mechanisms of one specific type (i.e., order).[5] At the other extreme the second type uses very sophisticated statistical methods which

can treat even data from complex reactions (i.e., reactions whose mechanisms involve more than one pathway from reactant to product, and in some cases involve steady state intermediates and equilibria). The latter type evaluates the non-linear equations involved in complex reactions by iterative methods, which necessitate the use of large, high speed computers.[6-8]

The programs presented here fill the gap that we feel exists between the two above-mentioned types of programs. They provide programming whose logic is readily understandable to the chemist who will be using them, and whose simplicity results in reduced machine code, core, and time. They establish the rate constants and order for irreversible reactions of known stoichiometry, such as the triarylmethane ion reaction, with little or no restriction on reaction order.

To present the programs a brief description of chemical kinetics and its terminology is given as background.[9] Then the programs written specifically for our work with the fading rates of UV activated photochromic triarylmethane leuconitriles, but applicable to most kinetic problems, can be discussed.

2. DISCUSSION

a. Definitions

The rate of a reaction is expressed in terms of the amount of any reactant or product of the reaction. It is usually expressed as change in amount, i.e., concentration or pressure, per unit time. Rates in solution are expressed as moles liter^{-1} sec^{-1} or moles cc^{-1} sec^{-1}.

The rate constant(k), which is also known as the specific rate and as the rate coefficient, is equivalent to reaction rate when the reactants

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are present at unit concentrations. The rate constant is a function of temperature, pressure, and the composition of the reactant mixture, and, therefore, indirectly a function of time. In stating a rate or rate constant it is necessary to express not only the concentration units, but also, the substance, the reactant or product, to which the rate refers.

The order of a reaction indicates the manner in which the reaction rate varies with the concentrations of the reacting substances. The order is found experimentally by determining the proportionality between the rate and the power of the concentration of each reactant. The overall reaction order is the sum of the powers of all the reactant concentrations which influence the rate.

Thus, for a reaction of the following stoichiometry

$$mA + nb \longrightarrow sC$$
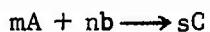
we see the rate can be expressed by the changes in concentration:

$$v = -\frac{1}{m} \frac{d(conc_A)}{dt} = -\frac{1}{n} \frac{d(conc_B)}{dt} = \frac{1}{s} \frac{d(conc_C)}{dt} \qquad (1)$$

or

$$v = k \ (conc_A)^a \ (conc_B)^b \ (conc_C)^c = k_A \ (conc_A)^a \ k_B \ (conc_B)^b \ k_C \ (conc_C)^c \qquad (2)$$

where   k = rate constant
v = rate
order of reaction = a + b + c

This equation (eq. 2) is the rate law for this particular reaction. In general, the form of the rate law is determined by experiment and cannot be predicted from the stoichiometric equation for the overall reaction. Usually reactions occur by complex mechanisms which lead to kinetic laws completely

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different from the stoichiometry. However, in the usual case where a reaction occurs in a single step, there is generally a relation between order and stoichiometry.

b. The Method of Integration

The rate of a chemical reaction is usually not measured directly, instead, the change in concentration of one of the reactants or products is determined as a function of time. The most widely employed method of determining the reaction order and rate, the method of integration, can then be applied.

The rate of a reaction may be related to the concentration of one reactant by holding all other concentrations constant. The constant k then includes these other concentrations, and equation (2) becomes:

$$v = k \ (conc)^n \tag{3}$$

where v = rate observed
k = rate constant
n = order (with respect to one reactant)

If for ease of integration, concentration is expressed as $a_0 - x$ (where a_0 is the initial concentration and x is the amount of a reactant consumed in time t), the integrated form shown in Table I of the rate equations for different orders can be found.

The reaction order is determined in this method by comparison of the experimental results with the results calculated for the integrated rate equations for reactions of different orders. If, as determined by trial and

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error, the kinetic data "fits" one of these integrated equations, (i.e.,
matches a calculated curve closely), it is concluded that the equation
chosen is applicable. The rate constant, k, is obtained for this order re-
action, usually by putting the integrated rate equation into such a form that
a linear plot, time versus some measure of concentration (see Table I,
column 3), is obtained. The fact that this second plot is linear is a fur-
ther indication of a good fit, and the slope (k) can be found by the method
of least squares.

The method of integration has two faults: (1) the results are con-
strained to fit the best integral-order law of those considered, even if
there might be a better fit with some other order and (2) the reaction is
characterized according to the way the concentration of <u>one</u> reactant or product
varies with time. This technique may lead to misleading conclusions about
the way the rate varies with the concentration of the other reactants
present in the system.

c. The Method of Differentiation

The differential method is used to measure the true order and the
initial rate without any preconditions. From these one can determine the
absolute rate constant.

The differential method is based on the fact that equation (3) can
also be expressed in logarithmic terms:

$$\log v = \log k + n \log c \tag{4}$$

For a curve showing the variation of one reactant with time, the
slope at any given time and concentration is the reaction velocity at that

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point. Therefore, a double-logarithmic plot of this velocity against concentration should give a straight line whose slope is the order of the reactant and whose intercept is the log of the rate for that order reaction.

The initial rate (i.e., initial slope) of a number of runs with different concentrations of a reactant can be used to give one value for n, called the order with respect to concentration (n_c), or the true order. Alternatively, measurement of the rate at different times (the slopes at different concentrations) during one run can be used to give another value for n, called the order with respect to time (n_t). These two orders are not always the same. An abnormally large difference can mean the reaction is inhibited ($n_c < n_t$) or autocatalytic ($n_c > n_t$). Both of these effects are due to interaction of products with the reactants.

d. The Isolation Method

If in a reaction system all the reactants but one are present in large excess, the apparent order of the reaction will be the order with respect to the one reactant which is "isolated." This isolated reactant is the only one which will change significantly in concentration during the course of the reaction. However, as with all these techniques, care should be taken since a complex reaction may undergo mechanistic changes influenced by concentration changes, and the results may be unreliable.

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3. FORTRAN IV PROGRAMMING

a. The Program for the Method of Integration

This program analyzes the kinetic data (i.e., the time vs. a changing variable) in four steps. The first step, a first order rate determination by least square linear regression analysis, is optional; and can be suppressed by use of the proper indicator. This optional first order rate analysis is available and is printed particularly for use in conjunction with the isolation method.

In the second step of the program, the rates at various times for all the orders under study are calculated in the same manner, using expressions such as those found in Table I. Tables are thereby generated for the rates at different stages of the reaction assuming, for the sake of trial, that, of the expressions for 0, 1/2, 1, 3/2, 2, and 3 order reactions, only one is valid for the experimental data. From these tables, the order whose rates at various times give the lowest coefficient of variance is selected as the order which fits the experimental data.

In the third step, the best order having been selected, a least square analysis is used to determine the rate of the reaction for the selected order, the slope of the line being obtained by plotting time against the right side of the integrated rate expression for the selected order

$$(e.g., \quad \frac{1}{n-1} \left[\frac{1}{(a_0 - x)^{n-1}} - \frac{1}{a_0^{n-1}} \right] \quad \text{where } n \neq 1).$$

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Finally, if a value for another reactant is introduced, the integrated rate expression for the reaction (a + b = c)* (a second order mechanism which is first order in a and b) is treated tabularly and by least square analysis as described above, to determine this second order rate.

In this way the program will analyze data (1) to give a first order rate constant for one reactant for use if desired with the isolation method; (2) to determine which of the trial orders gives a fit and determine the best rate for this order; (3) to calculate, if it is desired, a rate for a second order reaction which is first order in two reactants.

$$\frac{dX}{dt} = kab = k(a_0 - x) \ (b_0 - x), \text{and } kt = \frac{1}{b_0 - a_0} \ \ln \left[\frac{a_0 \ (b_0 - x)}{b_0 \ (a_0 - x)} \right] \quad (5)$$

b. The Program for the Method of Differentiation

This program treats the kinetic data in four steps to determine the order. First, a relation between time and concentration is determined either by linear regression with transformation of variables (e.g., exponential, inverse, or semilogarithmic curve fit) or by a third order polynomial regression. Goodness of fit is evaluated by the use of standard errors, and the equation which gives the best fit for the experimental data is used for the subsequent steps.

This equation is then used in the second step to derive the slope, or reaction velocity, at various times including the initial time. Linear least

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*Where the initial concentrations of a and b are not equal

squares analysis is carried out on the logarithms of these slopes versus

concentrations at various times. The slope of this regression line gives

the order with respect to time. Next, for any series of runs which differ

only in the concentration of the reactant of interest, the initial slopes

and initial concentrations for the series are treated to determine a value

from the slope of the regression line for the true order n_c.

Finally, for each of these series, n_c and the average value of n_t

are compared. If they differ to a significant extent ($>$ 0.1), the re-

action is labeled either autocatalytic or inhibited, as described on page 6

above.

In this way, the programs analyze kinetic data using the three most

common methods of chemical kinetics to determine the order and rate of re-

action. From this analysis one should gain a better understanding of the

relation between rate and various other factors of the reaction under study.

This knowledge hopefully would lead to a reaction mechanism which will be of

practical value in connection with technical problems.

4. PROGRAM LIMITATIONS

The two programs are designed (essentially) to treat the same set of

input data. The input consists of a variable (such as concentration)

measured at different times. A maximum of twenty time and variable data

points can be analyzed. The value of the variable must be greater than zero

and must not exceed nine significant figures.

5. INPUT, OUTPUT, AND GLOSSARY OF TERMS

a. Method of integration program

Input - from punched cards

1. Number of Runs Card   FORMAT(I3)

Column	Variable
1-3	NRUNS*

2. Run Control Card   FORMAT(2I3,6A5)

1-3	N*	No. of Points
4-6	N1*	Indicator 1 = ON 0 = OFF
7-36	CPD (II), II = 1,6	Run Name

3. Data Cards   FORMAT(8F20.4)

1-20,21-40,21-60,etc.	TIM (II), II = 1,N
1-20,21-40,41-60,etc.	ATA(II), II = 1,N

4. Concentration of Second Reactant   FORMAT (F20.4)

1-20	PO

Output - on printer

For each set of data the output appears as:

GIVEN THE FOLLOWING XX DATA POINTS FOR

TIME (SEC)	VARIABLE
XXXXX.XX	$\pm 0.XXXXE \pm XX$

---

*Right justified

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With the N1 indicator on, the program output from the first order kinetic

subroutine continues with:

ASSUMING FIRST ORDER KINETICS, THE RATES ARE

XXXXX.XX   ±0.XXXXE±XX

MEAN VALUE   ±0.XXXXE±XX

USING STRAIGHT LINE CURVE FITTING PROGRAM - RATE IS ±0.XXXXE±XX AND INTERCEPT

IS ±0.XXXXE±XX

Then at the top of the next page the main program continues:

CONSIDERING THIS ORDER WHICH GIVES THE LOWEST COEFFICIENT OF VARIANCE AS THE

BEST FIT, IT IS FOUND THAT WITH A STANDARD DEVIATION OF ±0.XXXXE±XX AND A

COEFFICIENT OF VARIANCE OF ±0.XXXXE±XX THE DATA FITS A

XX ORDER OF RATE EQUATION GIVING A MEAN RATE OF ±0.XXXXE±XX FROM -

XXXXX.XX   ±0.XXXXE±XX

APPLYING A LEAST SQUARES CURVE FIT TO THIS DATA

THE RATE IS ±0.XXXXXE±XX

If none of the integrated rate equations have a reasonable coefficient

of variance (less than 10) the preceding section is replaced by:

THIS DATA IS NOT CONSISTENT WITH ANY OF THE ONE COMPOUND RATE EQUATIONS.

The output then continues with the rates as calculated from all the integrated

equations:

TIME	ZERO ORDER	HALF ORDER	FIRST ORDER	3/2 ORDER	2ND ORDER	3RD ORDER
XXXXXX	±0.XXXXE±XX	±0.XXXXE±XX	±0.XXXXE±XX	±0.XXXXE±XX	±0.XXXXE±XX	±0.XXXXE±XX

If a value for B_0 was input (B_0 not equal 0), then the output from a second order (First in A and B) gives:

CALCULATION OF RATE FOR A REACTION FIRST ORDER IN A AND B WITH AN INITIAL

B OF $\underline{+}0.XXXXE\underline{+}XX$

TIME (SEC)	VARIABLE
XXXXX.XX	$\underline{+}0.XXXXE\underline{+}XX$

followed by the Mathpac FIT SUBROUTINE to give a first degree polynomial

curve fit for a value of the rate which is output as:

APPLYING A LEAST SQUARES CURVE FIT TO THIS DATA THE RATE IS $\underline{+}0.XXXXXE\underline{+}XX$

However, if the value input for B_0 is the same as A_0, the output from this subroutine becomes:

INITIAL A AND B ARE EQUAL -- SEE SECOND ORDER RATES.

After the last run has been processed, END OF PROGRAM is typed on the typewriter.

Glossary of Terms

Variable	Description
A1,A2,A3,A4,A5	Dummy arrays for MATHPAC/200 SUBROUTINE FIT
ADTA(I), I = 1,N	Variable data
TIME (I), I = 1,N	Time data
B0	Value of initial concentration of B
K(5,I), I = 1,N	Value of rate constants for orders at various times
XX(I), I = 1,N	Value of K(5,I) at XTIME(I)
CPD(I)	Name of run
R(I), I = 1,N	Second order rate values times TIME(I)
C	A test value (ADTA(I) - B0)
ABR	A second order rate value

Variable	Description
AN	N
X	XX
XS	Sum of X (XX) values
SX2	Sum of Values of TIME(I) squared
SX	Sum of values for all XX(I) times TIME(I)
SY	Sum of all rates times TIME(I) at various times
S2X	SX times SX
SXX	X times X summed
AMEAN	Mean Average of all first order rates at the various times
BOT	(AN x SX2) - S2X
A	Slope of linear curve fit
B	Intercept of linear curve fit
NRUNS	Number of Runs
N	Number of Points
N1	Indicator to carry out first order linear curve fit
IQ	
I	
KK	
K	
KL	
JJ	General Indices
II	
J	
LL	
MM	
JK	

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Variable	Description
SLOF	First Order Rate Linear Curve Fitting Subroutine
SDEV	Standard Deviation Subroutine
SORD	Second Order Rate-determining Subroutine for two Reactants
QFIT	Subroutine to Choose Best Order by Lowest Coefficient of Variance

b. Method of Differentiation Program.

Input - from punched cards

1. Number of Concentrations Card   FORMAT (I3)

Column	Variable
1-3	NCONC*

2. Number of Runs Card   FORMAT (I3)

1-3	NRUNS*

3. Run Control Card   FORMAT(I3,3X,6A5,9X,I5)

1-3	NPTS*
6-36	CPD(I), I = 1,6
46-50	INDC*

4. Data Cards   FORMAT(4F20.4)

1-20, 21-40, 41-60, etc.	TIME(I), I = 1,NPTS
1-20, 21-40, 41-60, etc.	ADTA(I), I = 1,NPTS

Output - on printer

As in the integration method, the run and time versus variable data are listed. Then the four curve fitting subroutines each print the attempted curve fit, the best fitting equation for that type, and except in the case of the polynomial, the equation for the slope. Following each equation, a table of the input and the calculated results from the fitted equation are printed for comparison.

* Right justified.

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The output is:

INVERSE FUNCTION CURVE FIT

THIS FITS CONC = $1/(\pm 0.XXXXE\pm XX + \pm 0.XXXXE\pm XX$ TIME) AND

$$SLOPE = -(\pm 0.XXXXE\pm XX)(\pm 0.XXXXE\pm XX + \pm 0.XXXXE\pm XX TIME)^{-2}$$

and the table:

TIME	VARIABLE	CALC. VAR.	CALC. SLOPE
$\pm 0.XXXXE\pm XX$	$\pm 0.XXXE\pm XX$	$\pm 0.XXXXE\pm XX$	$\pm 0.XXXYE\pm XX$

SE = $\pm 0.XXXXXE\pm XX$

EXPONENTIAL CURVE FIT

THE FIT GIVES $\pm 0.XXXXE\pm XX$ $\quad \text{TIME}^{(\pm 0.XXXXE\pm XX)}$

AND SLOPE = $(\pm 0.XXXXE\pm XX)(\pm 0.YXXXE\pm XX)$ TIME

followed by a table like above.

SEMILOG CURVE FIT

THIS FITS CONC = $10^{(\pm 0.XXXXE\pm XX + \pm 0.XXXE\pm XX \text{ TIME})}$ AND

SLOPE = $(2.303)(CONC)(\pm 0.XXXXE\pm XX)$

followed by a table like above.

POLYNOMIAL CURVE FIT

THE COEFFICIENTS OF THE POLYNOMIAL ARE

$\pm 0.XXXXXE\pm XX$ across four times followed by a table as above.

THE FIT CLOSEST TO THE DATA IS

If any of the first three subroutines give the lowest standard error

they are relisted. If the semilogarithmic gives the best fit, then the

output is:

SEMILOGARITHMIC CURVE FIT

and continuing in all cases:

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THE DERIVATIVE OF THIS EQUATION GIVES

TIME	SLOPE	LOG SLOPE	LOG VARIABLE
XXXXX.XXXX	$\pm$0.XXXXE$\pm$XX	$\pm$0.XXXXE$\pm$XX	$\pm$0.XXXXE$\pm$XX

At this point a polynomial curve fit by the built-in MATHPAC/200 FIT

SUBROUTINE outputs coefficients, variance and standard error for the

linear regression fit on the data. The program continues with:

FROM THIS THE ORDER WITH RESPECT TO TIME

   N_t = $\pm$0.XXXXXE$\pm$XX

WITH K = $\pm$XXXXXE$\pm$XX

If the time order indicator is on, the program will now print the logarithms

of initial concentration and slope:

   CONSIDERING THE XX PREVIOUS RUNS TO CALCULATE THE TRUE ORDER

VARIABLE	INITIAL SLOPE
$\pm$0.XXXXE$\pm$XX	$\pm$0.XXXXE$\pm$XX

Again, the MATHPAC/200 SUBROUTINE does a first order fit to the data

printing coefficients, variance, and standard error. Then the output continues:

FROM THIS THE ORDER WITH RESPECT TO CONCENTRATION

   N_c = $\pm$0.XXXXXE$\pm$XX

WITH K = $\pm$0.XXXXXE$\pm$XX

If the value differs by greater than 0.1 from the average N_t already

calculated for the previous runs,

THE DATA INDICATES THE REACTION TO BE AUTOCATALYTIC (INHIBITED).

THE TRUE ORDER IS $\pm$0.XXXXXE$\pm$XX

After the last set of data has been processed, END OF PROGRAM is typed

on the typewriter.

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Glossary of Terms

Variable	Description
A1,A2,A3,A4,A5	Dummy Arrays for MATHPAC/200
	SUBROUTINE FIT
ADTA(I),I = 1,NPTS	Variable data
TIME (I), I = 1,NPTS	Time data
LDATA(I), I = 1,NPTS	Logarithm of the variables
LTIME (I), I = 1,NPTS	Logarithm of the time
SE(I), I = 1,4	Standard Errors
X(I), I = 1,NPTS	Calculated Variables
CPD(6)	Run Name
SLOPE(I), I = 1,NPTS	Calculated slopes
SIN(30)	Logarithms of initial slopes
CONC(30)	Logarithms of initial variables
TEST	A test value
VAR	Variance
DT	Average value of n_t for runs of one concentration set
Y	Unsubscripted temporary location for TIME (I)
NC	Order with respect to concentration
NT	Order with respect to time
NPTS	Number of data points in each run
NRUNS	Number of runs at each concentration
D	Storage for difference between $n_c = n_t$ and also n_c

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Variable	Description
NCONC	Number of concentrations to be analyzed
INDNC	Indicator for determination of n_c, 0 = off, 1 = on
II	
IP	
	General Indices
IQ	
L	
POLYN	
SEMILG	Curve fitting subroutines
INVY	
EXPCF	
ERROR	A subroutine to calculate standard error

TABLE I

Special Cases of Integrated Rate Equations

Order	Differential Equations	Definite Integral
0	$\dfrac{dx}{dt} = k$	$kt = x$
1/2	$\dfrac{dx}{dt} = k (a_0 - x)^{\frac{1}{2}}$	$kt = 2 \left[a_0^{-\frac{1}{2}}(a_0 - x)^{-\frac{1}{2}} \right]$
1	$\dfrac{dx}{dt} = k (a_0 - x)$	$kt = \ln \left[a_0/(a_0 - x) \right]$
3/2	$\dfrac{dx}{dt} = (a_0 - x)^{3/2}$	$kt = 2 \left[(a_0 - x)^{\frac{1}{2}} - (a_0)^{\frac{1}{2}} \right]$
2	$\dfrac{dx}{dt} = k (a_0 - x)^2$	$kt = x/\left[a_0 (a_0 - x) \right]$
2	$\dfrac{dx}{dt} = k (a_0 - x) (b_0 - x)$	$kt = \dfrac{1}{b_0 - a_0} \ln\left[\dfrac{a_0 (b_0 - x)}{b_0 (a_0 - x)} \right]$
3	$\dfrac{dx}{dt} = k (a_0 - x)^3$	$kt = 1/2\left[\dfrac{2a_0 x - x^2}{a_0 (a_0 - x)^2} \right]$

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APPENDIX A

THE PROGRAM FOR THE METHOD OF INTEGRATION

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$JOB   NOGD
$ZE
$FORTRAN
C     A RATE AND ORDER DETERMINING PROGRAM USING LEAST SQUARE ANALYSIS
C     OF DATA   INPUT CONSISTS OF TIME VS REACTANT CONC.
C     THIS PROGRAM CAN ALSO CALCULATE RATES OF A REACTION FIRST ORDER IN
C     A AND IN B.  THE INITIAL B MUST BE INPUT FOLLOWING THE CHANGE IN A
C     DATA.
      COMMON A1(8),A2(20),A3(20),A4(20),A5(20),INO,AVG,R(20)
      COMMON E
      DIMENSION K(6,20),XX(20),TIME(20),ADTA(20),AVG(6),CPD(6)
      REAL K
      DATA K,XX/140*0./
    1 FORMAT(2I3,6A5)
    2 FORMAT(4F20.4)
    3 FORMAT(1H1,19HGIVEN THE FOLLOWING,1X,I3,1X,15HDATA POINTS FOR/6A5/
     3)
    4 FORMAT(5X,9HTIME(SEC),9X,8HVARIABLE/)
    5 FORMAT(4X,F8.2,10X,E11.4)
    6 FORMAT(1H0,16HTHE DATA FITS A ,I2,1X,45HORDER OF RATE EQUATION GIV
     1ING A MEAN RATE OF ,E11.4,1X,5HFRDM=)
    7 FORMAT(/47HAPPLYING A LEAST SQUARES CURVE FIT TO THIS DATA//12X,12
     7HTHE RATE IS ,E12.5)
    8 FORMAT(1H0,61HTHERE ARE TOO FEW DATA PDINTS (LT 6) TO CARRY OUT A
     2CURVE FIT/)
    9 FOPMAT(1H0,66HTHIS DATA IS NOT CONSISTENT WITH ANY OF THE ONE CPO
     6RATE EQUATIONS/)
   12 FORMAT(1H0,36HLEAST SQUARE FIT TO THE FIRST DEGREE)
   14 FORMAT(90H TIME     ZERO ORDER    HALF OROER    FIRST DRDER    3/2
     7ORDER      2NO CROER    THIRD ORDER/)
   15 FORMAT(I6,3X,E11.4,3X,E11.4,3X,E11.4,3X,E11.4,3X,E11.4,3X,E11.4)
   16 FORMAT(1H1)
   18 FORMAT(15H END DF PROGRAM)
      READ 1, NRUNS
      OD 10 IQ=1,NRUNS
      READ 1, N,N1,(CPD(II),II=1,6)
      READ 2,(TIME(II),II=1,N)
      READ 2,(AOTA(JJ),JJ=1,N)
      READ 2,BO
      PRINT 3,N,(CPD(II), II=1,6)
      PRINT 4
      OO 33 II=1,N
   33 PRINT 5, TIME(II), ADTA(II)
      IF(N1.EQ.0) GO TO 34
      CALL SLCF(AOTA,TIME,N)
      PRINT 16
   34 DO 20 I=2,N
      X=ADTA(1)-AOTA(I)
  100 K(1,I)=AOTA(I)/TIME(I)
  112 K(2,I)=2.*(ADTA(1)*ADTA(1)-ADTA(I)**.5)/TIME(I)
  110 K(3,I)=ALOG(AOTA(1)/ADTA(I))/TIME(I)
  132 K(4,I)=2.*(ADTA(I)**(-.5)-ADTA(1)**(-.5))/TIME(I)
  120 K(5,I)=X/(TIME(I)*ADTA(1)*ADTA(I))
  130 K(6,I)=((2.*AOTA(1)*X)-X*X)/(2.*TIME(I)*AOTA(1)*ADTA(1)*AOTA(I)*AD
```

22
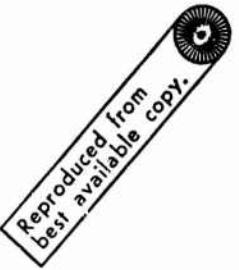
```
      STA(I))
   20 CONTINUE
      CALL QFIT(N,K,J)
      IF(IND.EQ.70) GO TO 91
      PRINT 6,IND,AVG(J)
      PRINT 5,(TIME(MM),K(J,MM), MM=1,N)
      IF(N-7)70,80,80
   80 DO 90 JK=2,N
      XX(JK)=K(J,JK)*TIME(JK)
   90 CONTINUE
      CALL FIT(A1,N,0,0,1,1,TIME,XX,A4,A5)
      PRINT 7, A1(2)
      PRINT 16
      GO TO 92
   70 PRINT 8
      GO TO 10
   91 PRINT 9
   92 PRINT 14
      PRINT 15,(TIME(I),K(1,I),K(2,I),K(3,I),K(4,I),K(5,I),K(6,I),I=1,N)
      IF(BO.EQ.0.) GO TO 10
      CALL SORD(N,TIME,ADTA,BO)
      IF((ADTA(1)-BO).EQ.0.) GO TO 10
      IF(E.LE.0.0)  GO TO 10
      CALL FIT(A1,N,0,0,1,1,TIME,R,A4,A5)
      PRINT 7, A1(2)
   10 CONTINUE
      TYPE 18
      STOP
      END


$FORTRAN
      SUBROUTINE SORD(N,TIME,ADTA,BO)
      COMMON A1(8),A2(20),A3(20),A4(20),A5(20),IND,AVG,R(20)
      COMMON E
      DIMENSION TIME(20),ADTA(20)
    4 FORMAT(5X,9HTIME(SEC),9X,8HVARIABLE/)
    5 FORMAT(4X,F8.2,10X,E11.4)
  225 FORMAT(1H0,79HCALCULATION OF RATE FOR A REACTION FIRST ORDER IN A
     5AND B WITH AN INITIAL B OF ,E10.4)
  226 FORMAT(50HINITIAL A AND B ARE EQUAL - SEE SECOND ORDER RATES//)
  227 FORMAT(1H0,17HBO IS LESS THAN X)
      PRINT 225,BO
      D=BO-ADTA(1)
      IF(D.EQ.0.)GO TO 221
      PRINT 4
      DO 220 I=2,N
      E=BO-ADTA(1)+ADTA(I)
      IF(E.LE.0.0) GO TO 230
      R(I)=(1./D)*ALOG((ADTA(1)*E)/(BO*ADTA(I)))
      ABR=R(I)/TIME(I)
      PRINT 5,TIME(I),ABR
  220 CONTINUE
      RETURN
```

23

```
  221 PRINT 226
      RETURN
  230 PRINT 227
      RETURN
      ENO


$FORTRAN
      SUBROUTINE QFIT(N,K,J)
      COMMON A1[8],A2[20],A3[20],A4[20],A5[20],IND,AVG,R[20]
      COMMON E
      DIMENSION K[6,20],SDEV[6],AVG[6]
      REAL K
      DATA SDEV/6*0./
    1 FORMAT[102HCONSIOERING THE ORDER WHICH GIVES THE LOWEST COEFFICIEN
     1T OF VARIANCE AS THE BEST FIT, IT IS FOUND THAT//]
    2 FORMAT[29HWITH A STANDARD DEVIATION OF ,E11.4,1X,33HAND A COEFFICI
     9ENT OF VARIANCE OF ,E11.4,20X,I3]
      PRINT 1
      B=FLOAT[N-1]
      DO 30 J=1,6
      VAR=0.
      SUM=0.
      IND=0
      DO 40 KK=2,N
   40 SUM=SUM+K[J,KK]
      AVG[J]=SUM/B
      OO 50 KL=2,N
   50 VAR=VAR+[AVG[J]-K[J,KL]]*[AVG[J]-K[J,KL]]
      SDEV[J]=SQRT[VAR/B]
   30 CONTINUE
      VAR=ABS[SDEV[1]/AVG[1]]
      OO 60 LL=2,6
      IF[ABS[SDEV[LL]/AVG[LL]].GT.VAR] GO TO 60
      VAR=ABS[SDEV[LL]/AVG[LL]]
      J=LL
   60 CONTINUE
      INO=[J-1]*5
      IF[IND.EQ.25] INO=30
      IF[ABS[VAR].GT.10.] IND=70
      PRINT 2, SOEV[J],VAR,IND
      RETURN
      ENO


$FORTRAN
      SUBROUTINE SLCF[ADTA,TIME,N]
      OIMENSION ADTA[20],TIME[20]
   11 FORMAT[1H0,49HUSING STRAIGHT LINE CURVE FITTING PROGRAM-RATE IS,1X
     3,E11.4,1X,17HANO INTERCEPT IS ,E11.4]
   15 FORMAT[1H0,45HASSUMING FIRST ORDER KINETICS, THE RATES ARE /]
   55 FORMAT[4X,F8.2,10X,E11.4]
   56 FORMAT[22X,11H-----------/7X,10HMEAN VALUE,5X,E11.4]
      AN=FLOAT[N-1]
```

24

```
                 XS=0.
                 SX2=0,
                 SX=0,
                 SY=0,
                 S2X=0,
                 SYX=0,
                 PRINT 13
                 DO 210 I=2,N
                 Y=ALOG(ADTA(1)/ADTA(I))
                 X=Y/TIME(I)
                 PRINT 55,TIME(I),X
                 XS=XS+X
                 SX2=SX2+TIME(I)*TIME(I)
                 SYX=SYX+Y*TIME(I)
                 SY=SY+Y
                 SX=SX+TIME(I)
            210 CONTINUE
                 S2X=SX*SX
                 AMEAN=XS/AN
                 BOT=AN*SX2-S2X
                 A=(AN*SYX-SX*SY)/BOT
                 B=(SX2*SY-SX*SYX)/BOT
                 PRINT 56,AMEAN
                 PRINT 11,A,B
                 RETURN
                 END
```

25

GIVEN THE FOLLOWING 20 DATA POINTS FOR
CVCN 10-4 CN 8,549X10-4 35C

TIME(SEC)	VARIABLE
0.00	0.1010E-04
1.00	0.9403E-05
2.00	0.8754E-05
3.00	0.8147E-05
4.00	0.7629E-05
5.00	0.7127E-05
6.00	0.6615E-05
7.00	0.6122E-05
8.00	0.5699E-05
9.00	0.5304E-05
10.00	0.4932E-05
11.00	0.4587E-05
12.00	0.4275E-05
13.00	0.3979E-05
14.00	0.3708E-05
15.00	0.3459E-05
16.00	0.3225E-05
17.00	0.3007E-05
18.00	0.2791E-05
19.00	0.2600E-05

ASSUMING FIRST ORDER KINETICS, THE RATES ARE

1.00	0.7190E-01
2.00	0.7171E-01
3.00	0.7176E-01
4.00	0.7024E-01
5.00	0.6981E-01
6.00	0.7060E-01
7.00	0.7158E-01
8.00	0.7158E-01
9.00	0.7161E-01
10.00	0.7172E-01
11.00	0.7179E-01
12.00	0.7168E-01
13.00	0.7168E-01
14.00	0.7160E-01
15.00	0.7146E-01
16.00	0.7137E-01
17.00	0.7129E-01
18.00	0.7147E-01
19.00	0.7144E-01
MEAN VALUE	0.7138E-01

USING STRAIGHT LINE CURVE FITTING PROGRAM-RATE IS 0.7158E-01 AND INTERCEPT IS -0.1395E-02

CONSIDERING THE ORDER WHICH GIVES THE LOWEST COEFFICIENT OF VARIANCE AS THE BEST FIT, IT IS FOUND THAT

WITH A STANDARD DEVIATION OF   0.5416E-03 AND A COEFFICIENT OF VARIANCE OF   0.7587E-02   10

THE DATA FITS A 10 ORDER OF RATE EQUATION GIVING A MEAN RATE OF   0.7138E-01 FROM-

0.00	0.0000E+00
1.00	0.7190E-01
2.00	0.7171E-01
3.00	0.7176E-01
4.00	0.7024E-01
5.00	0.6981E-01
6.00	0.7060E-01
7.00	0.7158E-01
8.00	0.7158E-01
9.00	0.7161E-01
10.00	0.7172E-01
11.00	0.7179E-01
12.00	0.7168E-01
13.00	0.7168E-01
14.00	0.7160E-01
15.00	0.7146E-01
16.00	0.7137E-01
17.00	0.7129E-01
18.00	0.7147E-01
19.00	0.7144E-01

APPLYING A LEAST SQUARES CURVE FIT TO THIS DATA

THE RATE IS 0.71560E-01

TIME	ZERO ORDER	HALF ORDER	FIRST ORDER	3/2 ORDER	2ND ORDER	THIRD ORDER
0	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
1	0.9403E-05	-0.6133E-02	0.7190E-01	0.2303E+02	0.7378E+04	0.7575E+09
2	0.4377E-05	-0.2959E-02	0.7171E-01	0.2339E+02	0.7631E+04	0.8135E+09
3	0.2716E-05	-0.1903E-02	0.7176E-01	0.2384E+02	0.7925E+04	0.8785E+09
4	0.1907E-05	-0.1381E-02	0.7024E-01	0.2373E+02	0.8027E+04	0.9233E+09
5	0.1425E-05	-0.1068E-02	0.6981E-01	0.2399E+02	0.8268E+04	0.9892E+09
6	0.1102E-05	-0.8573E-03	0.7060E-01	0.2474E+02	0.8700E+04	0.1088E+10
7	0.8746E-06	-0.7069E-03	0.7158E-01	0.2559E+02	0.9196E+04	0.1206E+10
8	0.7124E-06	-0.5968E-03	0.7158E-01	0.2607E+02	0.9562E+04	0.1312E+10
9	0.5893E-06	-0.5118E-03	0.7161E-01	0.2658E+02	0.9952E+04	0.1431E+10
10	0.4932E-06	-0.4442E-03	0.7172E-01	0.2714E+02	0.1038E+05	0.1566E+10
11	0.4170E-06	-0.3894E-03	0.7179E-01	0.2769E+02	0.1082E+05	0.1715E+10
12	0.3562E-06	-0.3446E-03	0.7168E-01	0.2818E+02	0.1125E+05	0.1872E+10
13	0.3061E-06	-0.3069E-03	0.7168E-01	0.2873E+02	0.1172E+05	0.2053E+10
14	0.2649E-06	-0.2751E-03	0.7160E-01	0.2925E+02	0.1219E+05	0.2248E+10
15	0.2306E-06	-0.2480E-03	0.7146E-01	0.2974E+02	0.1268E+05	0.2459E+10
16	0.2016E-06	-0.2245E-03	0.7137E-01	0.3028E+02	0.1319E+05	0.2699E+10
17	0.1769E-06	-0.2040E-03	0.7129E-01	0.3083E+02	0.1374E+05	0.2965E+10
18	0.1551E-06	-0.1856E-03	0.7147E-01	0.3155E+02	0.1441E+05	0.3294E+10
19	0.1368E-06	-0.1697E-03	0.7144E-01	0.3217E+02	0.1503E+05	0.3635E+10

CALCULATION OF RATE FOR A REACTION FIRST ORDER IN A AND B WITH AN INITIAL B OF 0.8549E-03

TIME(SEC)	VARIABLE
1.00	0.8414E+02
2.00	0.8395E+02
3.00	0.8404E+02
4.00	0.8229E+02
5.00	0.8181E+02
6.00	0.8276E+02
7.00	0.8394E+02
8.00	0.8397E+02
9.00	0.8402E+02
10.00	0.8418E+02
11.00	0.8428E+02
12.00	0.8417E+02
13.00	0.8420E+02
14.00	0.8412E+02
15.00	0.8398E+02
16.00	0.8389E+02
17.00	0.8381E+02
18.00	0.8404E+02
19.00	0.8402E+02

APPLYING A LEAST SQUARES CURVE FIT TO THIS DATA

THE RATE IS 0.84170E+02

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APPENDIX B

THE PROGRAM FOR THE METHOD OF DIFFERENTIATION

```
$JC9  NOGO
$F 'TRAN
      COMMON A116],A2[30],A3[30],A4[30],A5[30]
      COMMON LOATA[30],LTIME[30],SE[5],X[30]
      OIMENSION CPO[6],TIME[30],AOTA[30],LSLOPE[30],LAOTA[30],SIN[30],CO
     1NC[30],SLOPE[30]
      REAL LSLOPE, LAOTA, LOATA, LTIME
      EQUIVALENCE[LOATA,LAOTA]
    1 FORMAT[I3,3X,6A5,4X,F5.2,I5]
    2 FORMAT[4F20.4]
    3 FORMAT[1H1,19HGIVEN THE FOLLOWING,1X,I3,1X,15HOATA POINTS FOR/6A5/
     3]
    4 FORMAT[5X,9HTIME[SEC],9X,8HVARIABLE/]
    5 FORMAT[1H1,9X,33HTHE FIT CLOEST TO THE DATA IS THE]
    6 FORMAT[//38HTHE OERIVATIVE OF THIS EQUATION GIVES /24X,4HTIME,11X,
     65HSLOPE,9X,9HLOG SLOPE,6X,12HLOG VARIABLE/]
    7 FORMAT[21X,F10.4,5X,3[E11.4,5X]]
    8 FORMAT[/40HFROM THIS THE OROER WITH RESPECT TO TIME/13X,5HNT = ,E1
     82.5//9X,9HWITH K = ,E12.5]
    9 FORMAT[1H1,15HCONSIOERING THE,I4,42H PREVIOUS RUNS TO CALCULATE TH
     9E TRUE OROER/9X,8HVARIABLE,9X,13HINITIAL SLOPE/]
   10 FORMAT[7X,E11.4,8X,E11.4]
   11 FORMAT[/49HFROM THIS THE OROER WITH RESPECT TO CONCENTRATION/13X,5
     1HNC = ,E12.5//9X,9HWITH K = ,E12.5]
   12 FORMAT[//52HTHE OATA INDICATES THE REACTION TO BE AUTOCATALYTIC.]
   13 FORMAT[//48HTHE OATA INOICATES THE REACTION TO BE INHIBITEO.]
   14 FORMAT[//18HTHE TRUE OROER IS ,E12.5]
   15 FORMAT[5X,F10.4,6X,E12.5]
   16 FORMAT[30X,25HSEMILOGARITHMIC CURVE FIT//]
   17 FORMAT[21X,22HTHIS VARIABLE IS LE 0.///65H**NOTE** IF NC IS BEING
     7CALCULATED FOR THIS SET, IT IS INCORRECT.]
   18 FORMAT[15H ENO OF PROGRAM]
C
C     THE OIFFERENTIAL METHOO OF REACTION OROER OETERMINATION USING A
C     BEST CURVE FIT FROM EITHER INVERSE, EXPONENTIAL, POLYNOMIAL,OR
C     SEMILOGARITHMIC CURVE FITS.
C
      REAO 1, NCONC
      DO 1000 IP=1,NCONC
      REAO 1,NRUNS
      DT=0,
      OO 1000 IQ=1,NRUNS
      REAO 1, NPTS,[CPO[I],I=1,6],TH,INONC
      REAO 2,ITIME[I], I=1,NPTS]
      REAO 2,IAOTA[I], I=1,NPTS]
      PRINT 3, NPTS,[CPO[I], I=1,6]
      IF [NPTS.LT.5] GO TO 1000
      PRINT 4
      DO 33 II=1,NPTS
      IF[AOTA[II].LE.0.0] GO TO 60
   33 PRINT15, TIME[II], AOTA[II]
      CALL INVY[TIME,AOTA,NPTS,SLOPE]
      CALL EXPCF[TIME,AOTA,NPTS,SLOPE]
      CALL POLYN[TIME,AOTA,NPTS,SLOPE]
```

```fortran
      CALL SEMILG(TIME,ADTA,NPTS,SLOPE)
      PRINT 5
      L=1
      TEST=SE(1)
      DO 30 I=2,4
      IF(SE(I).GT.TEST) GO TO 50
      L=I
      TEST=SE(I)
   50 CONTINUE
      IF(L.EQ.1) CALL INVY(TIME,ADTA,NPTS,SLOPE)
      IF(L.EQ.2) CALL EXPCF(TIME,ADTA,NPTS,SLOPE)
      IF(L.EQ.3) CALL POLYN(TIME,ADTA,NPTS,SLOPE)
      IF(L.EQ.4) PRINT 16
      PRINT 6
      DO 20 I=1,NPTS
      IF(SLOPE(I).LT.0.) SLOPE(I)=(-1.)*SLOPE(I)
      LSLOPE(I)=ALOG10(SLOPE(I))
      LADTA(I)=ALOG10(ADTA(I))
      PRINT 7, TIME(I),SLOPE(I),LSLOPE(I),LADTA(I)
   20 CONTINUE
      CONC(IQ)=LADTA(1)
      SIN(IQ)=LSLOPE(1)
      CALL FIT(A1,NPTS,1,0,1,1,LADTA,LSLOPE,A4,A5)
      A1(1)=10.**A1(1)
      PRINT 8, A1(2),A1(1)
      DT=DT+A1(2)
      IF(INDNC.EQ.0) GO TO 1000
      IF(IQ.LT.3) GO TO 1000
      PRINT9, IQ
      PRINT 10, (CONC(I),SIN(I), I=1,NRUNS)
      CALL FIT(A1,IQ,1,1,_,1,CONC,SIN,A4,A5)
      A1(1)=10.**A1(1)
      PRINT 11,A1(2),A1(1)
      D=A1(2)-DT/FLOAT(IQ)
      IF(ABS(D).LT.0.1) GO TO 40
      IF(D.GT.0.) PRINT 12
      IF(D.LT.0.) PRINT 13
   40 D=(A1(2)+DT/FLOAT(IQ))/2.
      PRINT 14, D
      DT=0.
      GO TO 1000
   60 PRINT 17
 1000 CONTINUE
      TYPE 18
      STOP
      END
```

$FORTRAN
```fortran
      REAL FUNCTION ERROR(ADTA,X,NPTS)
      DIMENSION ADTA(30),X(30)
      VAR=0.
      DO 30 I=1,NPTS
   30 VAR=VAR+(ADTA(I)-X(I))*(ADTA(I)-X(I))
```

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```
        ERROR=SQRT(VAR/FLOAT(NPTS))
        RETURN
        END


SFORTRAN
        SUBROUTINE INVY(TIME,ADTA,NPTS,SLOPE)
C    INVERSE CURVE FIT
        COMMON A1(6),A2(30),A3(30),A4(30),A5(30)
        COMMON LDATA(30),LTIME(30),SE(5),X(30)
        DIMENSION TIME(30),ADTA(30),SLOPE(30)
        REAL LSLOPE, LADTA, LDATA, LTIME
        EQUIVALENCE(LDATA,LADTA)
    1 FORMAT(20HTHIS FITS CONC = 1/(,E11.4,3H + ,E11.4,10H TIME) AND/66X
     1,2H=2/11X,10HSLOPE = -(,E11.4,2H))(,E11.4,3H + ,E11.4,6H TIME)/)
    2 FORMAT(//12X,4HTIME,12X,8HVARIABLE,8X,9HCALC. VAR,5X,11HCALC. SLOP
     2E/)
    3 FORMAT(10X,4(E11.4,5X))
    4 FORMAT(//////16X,48HI N V E R S E   F U N C T I O N   C U R V E   F I
     4T/)
    6 FORMAT(//5HSE = ,E12.5)
        DO 10 I=1,NPTS
   10 LDATA(I)=1./ADTA(I)
        CALL FIT(A1,NPTS,0,0,1,1,TIME,LDATA,A4,A5)
        PRINT 4
        PRINT 1, A1(1),A1(2),A1(2),A1(1),A1(2)
        PRINT 2
        DO 20 I=1,NPTS
        X(I)=1./(A1(1)+A1(2)*TIME(I))
        SLOPE(I)=-A1(2)/X(I)**2
   20 PRINT 3, TIME(I),ADTA(I),X(I),SLOPE(I)
        N=NPTS-2
        SE(1)=ERROR(ADTA,X,N)                                    INVY
        PRINT 6, SE(1)
        RETURN
        END


SFORTRAN
        SUBROUTINE EXPCF(TIME,ADTA,NPTS,SLOPE)
C EXPONENTIAL CURVE FIT
        COMMON A1(6),A2(30),A3(30),A4(30),A5(30)
        COMMON LDATA(30),LTIME(30),SE(5),X(30)
        DIMENSION TIME(30),ADTA(30),SLOPE(30)
        REAL LDATA,LADTA
        EQUIVALENCE (LDATA,LADTA)
    1 FORMAT(////16X,39HE X P O N E N T I A L   C U R V E   F IT)
    2 FORMAT(//12X,4HTIME,12X,8HVARIABLE,8X,9HCALC. VAR,5X,11HCALC. SLOP
     2E/)
    3 FORMAT(10X,4(E11.4,5X))
    5 FORMAT(/27X,E11.4/14HTHE FIT GIVES ,E11.4,6H TIME //42X,1HI,E11.4,
     55H =1,I/13HAND SLOPE = (,E11.4,2H))E11.4,6HI TIME//)
    6 FORMAT(//5HSE = ,E12.5)
        DO 50 I=1,NPTS
```

```
      LDATA(I)=ALOG10(AOTA(I))
      IF(TIME(I).EQ.0.) TIME(I)=0.000001
      LTIME(I)=ALOG10(TIME(I))
   50 CONTINUE
      CALL FIT(A1,NPTS,0,0,1,1,LTIME,LDATA,A4,A5)
      PRINT 1
      A1(1)=1C.**A1(1)
      PRINT 5, A1(2),A1(1),A1(2),A1(1),A1(2)
      PRINT 2
      DO 20 I=1,NPTS
      X(I)=A1(1)-TIME(I)**A1(2)
      SLOPE(I)=A1(1)*A1(2)*TIME(I)**(A1(2)-1.)
   20 PRINT 3, TIME(I),ADTA(I),X(I),SLOPE(I)
      N=NPTS-2
      SE(2)=ERROR(ADTA,X,N)                                          EXPCF
      PRINT 6, SE(2)
      IF(TIME(1).EQ.0.000001) TIME(1)=0.0
      RETURN
      END


$FORTRAN
      SUBROUTINE POLYN(TIME,ADTA,NPTS,SLOPE)
C  POLYNOMIAL CURVE FIT
      COMMON A1(6),A2(30),A3(30),A4(30),A5(30)
      COMMON LOATA(30),LTIME(30),SE(5),X(30)
      DIMENSION TIME(30),AOTA(30),SLOPE(30)
    1 FORMAT(38HTHE COEFFICIENTS OF THE POLYNOMIAL ARE/6(E12.5,3X)/)
    2 FORMAT(//12X,4HTIME,12X,8HVARIABLE,8X,9HCALC. VAR,5X,11HCALC. SLOP
     2E/)
    3 FORMAT(10X,4(E11.4,5X))
    4 FORMAT(////16X,37HP O L Y N O M I A L  C U R V E  F I T/)
    5 FORMAT(1H0,30X,20HPOLYNOMIAL CURVE FIT/24X,26HCANNOT BE CARRIED OU
     5T WITH,I2,7H POINTS)
    6 FORMAT(//5HSE = ,E12.5)
      IF(NPTS.LE.6) GO TO 30
      CALL FIT(A1,NPTS,0,0,3,3,TIME,AOTA,A4,A5)
      PRINT 4
      PRINT 1, (A1(I), I=1,4)
      PRINT 2
      DO 20 I=1,NPTS
      Y=TIME(I)
      X(I)=A1(1)+A1(2)*Y+A1(3)*Y*Y+A1(4)*Y**3+A1(5)*Y**4
      SLOPE(I)=(A1(2)+2.*A1(3)*Y+3.*A1(4)*Y*Y+4.*A1(5)*Y**3)
   20 PRINT 3, TIME(I),ADTA(I),X(I),SLOPE(I)
      N=NPTS-4
      SE(3)=ERROR(AOTA,X,N)                                          POLYN
      PRINT 6, SE(3)
      RETURN
   30 PRINT 5, NPTS
      SE(3)=SE(2)+SE(1)
      RETURN
      END
```

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```
$FORTRAN
      SUBROUTINE SEMILG(TIME,ADTA,NPTS,SLOPE)
C SEMILOG CURVE FIT
      COMMON A1(6),A2(30),A3(30),A4(30),A5(30)
      COMMON LDATA(30),LTIME(30),SE(5),X(30)
      DIMENSION TIME(30),ADTA(30),SLOPE(30)
      REAL LDATA,LADTA
      EQUIVALENCE (LDATA,LADTA)
    1 FORMAT(///19X,1H(,E11.4,3H + ,E11.4,6H TIME)/19HTHIS FITS CC C = 1
     10,33X,26HAND SLOPE = )2.303))CONC)),E11.4,1H)/(
    2 FORMAT)//12X,4HTIME,12X,8HVARIABLE,8X,9HCALC. VAR,5X,11HCALC. SLOP
     2F/)
    3 FORMAT)10X,4)E11.4,5X()
    4 FORMAT)//////16X,31HS E M I L O G   C U R V E   F I T)
    6 FORMAT(//5HSE = ,E12.5)
      DO 10 I=1,NPTS
   10 LDATA(I)=ALOG10(ADTA(I))
      CALL FIT(A1,NPTS,0,0,1,1,TIME,LDATA,A4,A5)
      PRINT 4
      PRINT 1, A1(1),A1(3),A1(2)
      PRINT 2
      DO 20 I=1,NPTS
      X(I)=10.**(A1)1)+A1(2)*TIME(I))
      SLOPE(I)=A1(2)*X(I)*2.30259
   20 PRINT 3, TIME(I),ADTA(I),X(I),SLOPE(I)          SEMILOG
      N=NPTS-2
      SE(4)=ERROR)ADTA,X,N)
      PRINT 6, SE)4)
      RETURN
      END
```

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GIVEN THE FOLLOWING 20 DATA POINTS FOR
CVCN 10-4 CN 8.549X10-4 35C

TIME(SEC)	VARIABLE
0.0000	0.10100E-04
1.0000	0.94030E-05
2.0000	0.87540E-05
3.0000	0.81470E-05
4.0000	0.76290E-05
5.0000	0.71270E-05
6.0000	0.66150E-05
7.0000	0.61220E-05
8.0000	0.56990E-05
9.0000	0.53040E-05
10.0000	0.49320E-05
11.0000	0.45870E-05
12.0000	0.42750E-05
13.0000	0.39790E-05
14.0000	0.37080E-05
15.0000	0.34590E-05
16.0000	0.32250E-05
17.0000	0.30070E-05
18.0000	0.27910E-05
19.0000	0.26000E-05

I N V E R S E F U N C T I O N C U R V E F I T

THIS FITS CONC = 1/(0.7271E+05 + 0.1468E+05 TIME) AND

$$SLOPE = -(0.1468E+05)(0.7271E+05 + 0.1468E+05 TIME)^{-2}$$

TIME	VARIABLE	CALC. VAR	CALC. SLOPE
0.0000E+00	0.1010E-04	0.1375E-04	-0.7759E+14
0.1000E+01	0.9403E-05	0.1144E-04	-0.1121E+15
0.2000E+01	0.8754E-05	0.9798E-05	-0.1529E+15
0.3000E+01	0.8147E-05	0.8566E-05	-0.2000E+15
0.4000E+01	0.7629E-05	0.7609E-05	-0.2534E+15
0.5000E+01	0.7127E-05	0.6845E-05	-0.3132E+15
0.6000E+01	0.6615E-05	0.6220E-05	-0.3793E+15
0.7000E+01	0.6122E-05	0.5700E-05	-0.4517E+15
0.8000E+01	0.5699E-05	0.5260E-05	-0.5304E+15
0.9000E+01	0.5304E-05	0.4883E-05	-0.6155E+15
0.1000E+02	0.4932E-05	0.4556E-05	-0.7068E+15
0.1100E+02	0.4587E-05	0.4271E-05	-0.8045E+15
0.1200E+02	0.4275E-05	0.4019E-05	-0.9085E+15
0.1300E+02	0.3979E-05	0.3795E-05	-0.1019E+16
0.1400E+02	0.3708E-05	0.3595E-05	-0.1136E+16
0.1500E+02	0.3459E-05	0.3415E-05	-0.1259E+16
0.1600E+02	0.3225E-05	0.3252E-05	-0.1388E+16
0.1700E+02	0.3007E-05	0.3104E-05	-0.1523E+16
0.1800E+02	0.2791E-05	0.2969E-05	-0.1665E+16
0.1900E+02	0.2600E-05	0.2845E-05	-0.1814E+16

SE = 0.10519E-05

EXPONENTIAL CURVE FIT

0.6228E+00

THE FIT GIVES 0.4945E-05 TIME

(0.6228E+00 -1.)

AND SLOPE = (0.4945E-05)(0.6228E+00) TIME

TIME	VARIABLE	CALC. VAR	CALC. SLOPE
0.1000E-05	0.1010E-04	0.9069E-09	0.5648E-03
0.1000E+01	0.9403E-05	0.4945E-05	0.3079E-05
0.2000E+01	0.8754E-05	0.7614E-05	0.2371E-05
0.3000E+01	0.8147E-05	0.9801E-05	0.2035E-05
0.4000E+01	0.7629E-05	0.1172E-04	0.1825E-05
0.5000E+01	0.7127E-05	0.1347E-04	0.1678E-05
0.6000E+01	0.6615E-05	0.1509E-04	0.1567E-05
0.7000E+01	0.6122E-05	0.1661E-04	0.1478E-05
0.8000E+01	0.5699E-05	0.1805E-04	0.1405E-05
0.9000E+01	0.5304E-05	0.1943E-04	0.1344E-05
0.1000E+02	0.4932E-05	0.2075E-04	0.1292E-05
0.1100E+02	0.4587E-05	0.2201E-04	0.1246E-05
0.1200E+02	0.4275E-05	0.2324E-04	0.1206E-05
0.1300E+02	0.3979E-05	0.2443E-04	0.1170E-05
0.1400E+02	0.3708E-05	0.2558E-04	0.1138E-05
0.1500E+02	0.3459E-05	0.2670E-04	0.1109E-05
0.1600E+02	0.3225E-05	0.2780E-04	0.1082E-05
0.1700E+02	0.3007E-05	0.2887E-04	0.1058E-05
0.1800E+02	0.2791E-05	0.2992E-04	0.1035E-05
0.1900E+02	0.2600E-05	0.3094E-04	0.1014E-05

SE = 0.15528E-04

POLYNOMIAL CURVE FIT

THE COEFFICIENTS OF THE POLYNOMIAL ARE
0.10087E-04   -0.69831E-06   0.20940E-07   -0.25837E-09

TIME	VARIABLE	CALC. VAR	CALC. SLOPE
0.0000E+00	0.1010E-04	0.1009E-04	-0.6983E-06
0.1000E+01	0.9403E-05	0.9410E-05	-0.6572E-06
0.2000E+01	0.8754E-05	0.8772E-05	-0.6176E-06
0.3000E+01	0.8147E-05	0.8174E-05	-0.5796E-06
0.4000E+01	0.7629E-05	0.7613E-05	-0.5432E-06
0.5000E+01	0.7127E-05	0.7087E-05	-0.5083E-06
0.6000E+01	0.6615E-05	0.6596E-05	-0.4749E-06
0.7000E+01	0.6122E-05	0.6137E-05	-0.4431E-06
0.8000E+01	0.5699E-05	0.5709E-05	-0.4129E-06
0.9000E+01	0.5304E-05	0.5310E-05	-0.3842E-06
0.1000E+02	0.4932E-05	0.4940E-05	-0.3570E-06
0.1100E+02	0.4587E-05	0.4596E-05	-0.3314E-06
0.1200E+02	0.4275E-05	0.4277E-05	-0.3074E-06
0.1300E+02	0.3979E-05	0.3981E-03	-0.2849E-06

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                    0.1400E+02      0.3708E-05      0.3706E-05      -0.2639E-06
                    0.1500E+02      0.3459E-05      0.3452E-05      -0.2445E-06
                    0.1600E+02      0.3225E-05      0.3217E-05      -0.2267E-06
                    0.1700E+02      0.3007E-05      0.2998E-05      -0.2104E-06
                    0.1800E+02      0.2791E-05      0.2796E-05      -0.1956E-06
                    0.1900E+02      0.2600E-05      0.2607E-05      -0.1824E-06
```

SE = 0.15926E-07

S E M I L O G   C U R V E   F I T

$$\text{THIS FITS CONC} = 10^{(-0.4995E+01 + -0.3108E-01 \text{ TIME})} \quad \text{AND SLOPE} = (2.303)(CONC)(-0.3108E-01)$$

```
             TIME          VARIABLE        CALC. VAR       CALC. SLOPE

          0.0000E+00      0.1010E-04      0.1011E-04      -0.7238E-06
          0.1000E+01      0.9403E-05      0.9416E-05      -0.6738E-06
          0.2000E+01      0.8754E-05      0.8766E-05      -0.6272E-06
          0.3000E+01      0.8147E-05      0.8161E-05      -0.5839E-06
          0.4000E+01      0.7629E-05      0.7597E-05      -0.5436E-06
          0.5000E+01      0.7127E-05      0.7073E-05      -0.5061E-06
          0.6000E+01      0.6615E-05      0.6584E-05      -0.4711E-06
          0.7000E+01      0.6122E-05      0.6130E-05      -0.4386E-06
          0.8000E+01      0.5699E-05      0.5706E-05      -0.4083E-06
          0.9000E+01      0.5304E-05      0.5312E-05      -0.3801E-06
          0.1000E+02      0.4932E-05      0.4945E-05      -0.3539E-06
          0.1100E+02      0.4587E-05      0.4604E-05      -0.3294E-06
          0.1200E+02      0.4275E-05      0.4286E-05      -0.3067E-06
          0.1300E+02      0.3979E-05      0.3990E-05      -0.2855E-06
          0.1400E+02      0.3708E-05      0.3714E-05      -0.2658E-06
          0.1500E+02      0.3459E-05      0.3458E-05      -0.2474E-06
          0.1600E+02      0.3225E-05      0.3219E-05      -0.2303E-06
          0.1700E+02      0.3007E-05      0.2997E-05      -0.2144E-06
          0.1800E+02      0.2791E-05      0.2790E-05      -0.1996E-06
          0.1900E+02      0.2600E-05      0.2597E-05      -0.1858E-06
```

SE = 0.19311E-07

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THE FIT CLOEST TO THE DATA IS THE

P O L Y N O M I A L   C U R V E   F I T

THE COEFFICIENTS OF THE POLYNOMIAL ARE
0.1008E-04   -0.69631E-06   0.20940E-07   -0.25837E-09

TIME	VARIABLE	CALC. VAR	CALC. SLOPE
0.0000E+00	0.1010E-04	0.1009E-04	-0.6983E-06
0.1000E+01	0.9403E-05	0.9410E-05	-0.6572E-06
0.2000E+01	0.8754E-05	0.8772E-05	-0.6176E-06
0.3000E+01	0.8147E-05	0.8174E-05	-0.5796E-06
0.4000E+01	0.7629E-05	0.7613E-05	-0.5432E-06
0.5000E+01	0.7127E-05	0.7087E-05	-0.5083E-06
0.6000E+01	0.6615E-05	0.6596E-05	-0.4749E-06
0.7000E+01	0.6122E-05	0.6137E-05	-0.4431E-06
0.8000E+01	0.5699E-05	0.5709E-05	-0.4129E-06
0.9000E+01	0.5304E-05	0.5310E-05	-0.3842E-06
0.1000E+02	0.4932E-05	0.4940E-05	-0.3570E-06
0.1100E+02	0.4587E-05	0.4596E-05	-0.3314E-06
0.1200E+02	0.4275E-05	0.4277E-05	-0.3074E-06
0.1300E+02	0.3979E-05	0.3981E-05	-0.2849E-06
0.1400E+02	0.3708E-05	0.3706E-05	-0.2639E-06
0.1500E+02	0.3459E-05	0.3452E-05	-0.2445E-06
0.1600E+02	0.3225E-05	0.3217E-05	-0.2267E-06
0.1700E+02	0.3007E-05	0.2998E-05	-0.2104E-06
0.1800E+02	0.2791E-05	0.2796E-05	-0.1956E-06
0.1900E+02	0.2600E-05	0.2607E-05	-0.1824E-06

SE = 0.15926E-07

THE DERIVATIVE OF THIS EQUATION GIVES

TIME	SLOPE	LOG SLOPE	LOG VARIABLE
0.0000	0.6983E-06	-0.6156E+01	-0.4996E+01
1.0000	0.6572E-06	-0.6182E+01	-0.5027E+01
2.0000	0.6176E-06	-0.6209E+01	-0.5058E+01
3.0000	0.5796E-06	-0.6237E+01	-0.5089E+01
4.0000	0.5432E-06	-0.6265E+01	-0.5118E+01
5.0000	0.5083E-06	-0.6294E+01	-0.5147E+01
6.0000	0.4749E-06	-0.6323E+01	-0.5179E+01
7.0000	0.4431E-06	-0.6353E+01	-0.5213E+01
8.0000	0.4129E-06	-0.6384E+01	-0.5244E+01
9.0000	0.3842E-06	-0.6415E+01	-0.5275E+01
10.0000	0.3570E-06	-0.6447E+01	-0.5307E+01
11.0000	0.3314E-06	-0.6480E+01	-0.5338E+01
12.0000	0.3074E-06	-0.6512E+01	-0.5369E+01
13.0000	0.2849E-06	-0.6545E+01	-0.5400E+01
14.0000	0.2639E-06	-0.6579E+01	-0.5431E+01
15.0000	0.2445E-06	-0.6612E+01	-0.5461E+01
16.0000	0.2267E-06	-0.6645E+01	-0.5491E+01
17.0000	0.2104E-06	-0.6677E+01	-0.5522E+01
18.0000	0.1956E-06	-0.6709E+01	-0.5554E+01
19.0000	0.1824E-06	-0.6739E+01	-0.5585E+01

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NO. OBSERVATIONS   20
POLY. DEGREE   1

COEFFICIENTS

0   -0.11412282E+01
1   0.10012681E+01

ERR-SQD = 0.7205657E-03   STD-ERR = 0.6327039E-02

FROM THIS THE ORDER WITH RESPECT TO TIME
NT =   0.10013E+01

WITH K =   0.72239E-01

NO. OBSERVATIONS   3
POLY. DEGREE   1

COEFFICIENTS

0   -0.11593894E+02
1   -0.10981919E+01

RESIDUAL SUMMARY

POINT	X-VALUE	Y-VALUE	Y-CALC	Y-DIFF
1	-0.49956786E+01	-0.61559521E+01	-0.61076799E+01	-0.48272178E-01
2	-0.48099486E+01	-0.63057008E+01	-0.63116471E+01	0.59463233E-02
3	-0.50217738E+01	-0.60366965E+01	-0.60790224E+01	0.42325854E-01

ERR-SQD = 0.4157040E-02   STD-ERR = 0.6447511E-01

FROM THIS THE ORDER WITH RESPECT TO CONCENTRATION
        NC = +0.10982E+01

     WITH K = 0.25475E-11

THE DATA INDICATES THE REACTION TO BE INHIBITED.

THE TRUE ORDER IS -0.32182E-01